

Research article

Contribution of modified P-enriched biochar on pH buffering capacity of acidic soil

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ABSTRACT

Biochar can directly hold cations in soil because of the negative charge that exists on its surfaces. Besides, improving soil cation exchange capacity, the negative charges on biochar surfaces can buffer acid soil by protonation and deprotonation mechanisms. Moreover, biochar ameliorates soil acidity due to the presence of oxides, carbonates, and hydroxides of its basic cations (Ca, Na, K, and Mg). Both biochar surface functional group and basic cation concentrations can be altered by modification with chemical agents which can affect its soil pH buffering capacity. However, the impact of modified biochar application on soil pH buffering capacity is still scanty. This study investigated the pH buffering capacity of acidic soil amended with three P-enriched modified Douglas fir biochars and compared this buffering capacity to amendment with untreated Douglas fir biochar. These three P-enriched biochars, were prepared by treating Douglas fir biochar (DFB), respectively, with: 1) anhydrous calcium chloride (CaCl_2) and potassium phosphate monobasic (KH_2PO_4), 2) calcium carbonate (CaCO_3) and diammonium phosphate $\{(\text{NH}_4)_2\text{HPO}_4\}$ and 3) an aqueous solution of magnesium sulfate (MgSO_4), potassium hydroxide (KOH) and potassium phosphate monobasic (KH_2PO_4). The three P-enriched biochars were designated as CCPP, CAPP and MSPP, respectively. The soil pH buffering abilities were largely dependent on the added biochar's alkalinity and ash contents. The residual soil CEC was highly correlated ($r \geq 0.9$), with the soil buffering capacity. Both alkalinity and pH buffering capacity improved following the order CCAP > CCPP > MSPP > DFB, while residual soil CEC followed the order CAPP > MSPP > CCPP > DFB. The pH buffering capacity of the soil after amendments with 10% CAPP, CCPP MSPP and BFB rose by 84.8, 58.3, 3.0 and 2.5%, respectively. Whereas MSPP had higher concentrations of K^+ and Mg^{2+} , greater concentrations of Ca^{2+} were present in CCAP and CCPP than MSPP. So, Ca^{2+} concentrations in biochar exerts a greater influence on alkalinity and buffering capacity than Mg^{2+} and K^+ because of 1) its smaller effective hydration radius and larger charge density. 2) calcium hydroxide has a greater water solubility than magnesium hydroxide providing more available base. Since pH buffering capacity depends on cation exchange sites, soil additives containing Ca^{2+} are prone to create greater impacts than Mg^{2+} and K^+ additives.

1. Introduction

Soil acidification is a natural process that has been escalating because of anthropogenic activities (Xu et al., 2012). Soil acidity is caused by the dissociation of organic acids, acid deposition, continued application of ammonium-based nitrogen fertilizers and excess uptake of basic cations by plants versus replenishment rates (Barak et al., 1996; Goulding, 2016; Wortmann et al., 2009). Excessive soil acidification

affects plant growth by inducing nutrient deficiencies, especially those of phosphorus, calcium, magnesium, and molybdenum (Wortmann et al., 2009). Phosphorus and molybdenum deficiencies result from adsorption of nutrients present in soil solutions by clay minerals, iron oxides and aluminum oxides at low pH (<5), forming insoluble phosphates and molybdates (Nie et al., 2020; Martinsen et al., 2015). In addition, low soil pH induces increased solubility and plant uptake of heavy metals such as cadmium (Abedi and Mojiri, 2020; Wang et al.,

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2006). Furthermore, excessively acidic soil pH values can induce elemental toxicities in plants due to increased aluminum, iron, manganese, and zinc solubilities and uptake (Meng et al., 2019; Shetty and Prakash, 2020). Moreover, available plant nutrients (N, P, K) decline in acidic conditions because microbial activity deteriorates (Wortmann et al., 2009). This lowers nitrogen fixation and nutrient mineralization (mobilization) (Rashid et al., 2016). These two processes are vital for creating plant-available forms of nutrients. Therefore, managing soil pH is vital for maintaining agricultural productivity.

Conventionally, lime/limestone (calcium carbonate) (Shetty and Prakash, 2020) and similar compounds including dolomitic limestone (Gezahegn et al., 2019), quicklime, hydrated lime, marl, chalk, oyster shells, fluid lime (Mahler, 2004; Peters et al., 1996), and wood ashes (Neina et al., 2020) have been used to lower soil acidity. However, conventional liming agents are ineffective in improving subsurface soil acidity due to low solubility and slow movement into deeper soil depths (Li, 2018). Moreover, plants access to required nutrients amount in the critical yield-forming phase could be inhibited because of slow reaction of lime with soil to release fixed plant nutrients (Ameiyu, 2019). Extensive use of liming materials could cause supply shortages and inflated costs (Shi et al., 2019), limiting access to these agents to farmers in developing countries. Consequently, using biochar as a low-cost liming alternative for ameliorating soil acidity has been suggested (Domingues et al., 2017; Wang et al., 2014). Recently, Li (2018) suggested that simultaneous application of lime and organic material could facilitate downward movement of alkalinity.

Biochar is a carbonaceous material formed from pyrolysis of carbon-rich biomass under oxygen deficient or oxygen-free conditions (Gezahegn et al., 2019). Recently, research on biochar as a soil additive has increased due to its long term ability to improve soil physical, chemical and water retention properties (Gondim et al., 2018), microbial activity (Batista et al., 2018), ion exchange capacity and P retention and use efficiency (Martinsen et al., 2015; Mukherjee et al., 2011). Negative biochar surfaces can adsorb exchangeable soil cations (Tan et al., 2020; Waters et al., 2010). Moreover, negative biochar surface charges can buffer soil acidity (Wang et al., 2014). Biochar addition raises soil pH because metal cations compete with H^+ ions for cation exchange surface sites. (Gezahegn et al., 2019). Mg, Ca, Na and K embedded in biochar as oxides, carbonates and hydroxides hydrolyze to form hydroxide ions that increase soil pH. Moreover, binding phosphate to biochar has been shown to slow down phosphate release, making it a suitable alternative for sustainable agriculture (An et al., 2021). Excessive release of phosphate in the environment causes eutrophication of water bodies. In addition, phosphate treated biochar has been shown to exhibit greater heavy metal immobilization capacity from polluted soil than neat biochar. (Beatrice et al., 2022; Chen et al., 2020; Zhou et al., 2022). Soil was also amended with Hydroxyapatite/Calcium Silicate Hydrate (HAP/CSH) treated biochar (Chen et al., 2020). Heavy metal reduction increased with phosphate contents in the amendment material. Compared to the control, this work achieved Cd reduction of $\geq 27.7\%$. The improved heavy metal sorption by the Biochar Facilitated Hydroxyapatite/Calcium Silicate Hydrate (BC-HAP/CSH) was attributed to higher amounts of oxygen-containing functional groups such as carboxyl, hydroxyl, and carboxylate which gave additional adsorption sites for heavy metals (Chen et al., 2020). Furthermore, the use of P-enriched biochar could provide an eco-friendly approach to solid waste management. In addition to enhancing soil fertility, P-enriched biochar application sequesters carbon that would otherwise release toxic gases such as CO and CO_2 via combustion or decay (Ye et al., 2019).

Sequential modification and enrichment of a high surface area, porous Douglas fir biochar with magnesium chloride, potassium hydroxide and potassium dihydrogen phosphate, followed by addition to soil, improved soil pH and basic cation concentrations (Arwenyo et al., 2021). Thus, application of P-enriched biochar could be even more effective at buffering soil acidity than untreated biochar. This hypothesis

is untested. Therefore, we investigated the ability of P-enriched biochar to buffer soil acidity, while assuming this influence could depend on cations used in the modification. So, the study compared the effectiveness of untreated Douglas fir biochar to three P enriched Douglas fir biochar amendments, to ameliorate soil acidity by determining their ash alkalinity, electrical conductivity, nutrients content and base cations concentrations.

2. Methods and materials

A sandy surface soil (0–20 cm) was collected from the Mississippi State University research farm, air-dried, homogenized, ground, and sieved through 2 mm mesh before analysis. Prior to use, the soil was analyzed for physical and chemical properties (Table S1), following the Lancaster Soil Test method described by (Cox, 2001). The soil had a pH of 5.64. All chemicals used were analytical grade (Sigma Aldrich). The purpose of using different modifying agents was to assess if different modifications would enhance this Douglas fir biochar as a soil pH buffer. Basic soil cations include potassium, sodium, calcium, and magnesium. However, high sodium concentrations contribute to sodicity and salinity which can affect plant growth negatively (Kronzucker et al., 2013). Thus, three P-enriched biochars were prepared using K^+ , Ca^{2+} and Mg^{2+} . The first, designated as CCPP, was made using anhydrous calcium chloride and potassium dihydrogen phosphate as modifying agents. Calcium carbonate and diammonium phosphate were used to prepare CCAP. Finally, magnesium sulfate, potassium hydroxide and potassium dihydrogen phosphate were combined to make MSPP.

2.1. Origin of douglas fir biochar (DFB)

Douglas fir biochar is a commercial product (Black Owl Biochar, Biochar Supreme Inc.) obtained as a by-product from bio-syngas production. The production method, previously discussed by (Bomбуwala Dewage et al., 2018), included the introduction of green Douglas fir wood chips into an air-fed updraft wood gasifier at ~ 900 – $1000^\circ C$ for a residence time of ~ 1 – $30s$. The biochar had a relatively high surface area of $616 m^2/g$, low ash contents ($\sim 1.6\%$) and an alkaline pH (~ 8).

2.2. Preparation of P-enriched biochar

Prior to chemical modification treatments, Douglas fir biochar (DFB), was ground and sieved to a particle size $\leq 350 \mu m$. P-enriched biochar was obtained by treating the sieved Douglas fir biochar with 1) $CaCl_2$ and KH_2PO_4 (CCPP), 2) $CaCO_3$ and $(NH_3)_2HPO_4$ (CCAP) and 3) $MgSO_4$, KOH and KH_2PO_4 (MSPP).

2.2.1. Preparation of CCPP

DFB, $\sim 50 g$, ($\leq 350 \mu m$ particle size) and deionized water, 400 mL, were mixed in a beaker to a uniform slurry and heated to $37^\circ C$ with constant stirring. To this slurry, 25 g of anhydrous $CaCl_2$ was dissolved and stirred for 30 min. Then, 25 g of KH_2PO_4 was dissolved in this slurry, stirred and the pH was adjusted to 10 with 10 M KOH (aq.) with continued stirring for 2 h. The slurry was aged for 24 h at room temperature and then vacuum filtered through Whatman number 1 filter paper. The CCPP was washed four times each with 200 mL of deionized water, oven-dried at

~ 1 atm to constant weight (70.39 g) at $80^\circ C$ for 48 h and kept in an air-tight container until use.

2.2.2. Preparation of CCAP

To DFB, 50 g, and 400 mL of deionized water was stirred to a uniform slurry in a 1000 mL beaker. After warming to $60^\circ C$, 20 g of $CaCO_3$ was added and stirred for 30 min more. Then 13 g of diammonium phosphate was added. The resulting slurry was stirred continuously for 72 h at room temperature. The product (CCAP) was filtered, washed four times each with ~ 200 mL of deionized water, oven-dried at 1 atm pressure to

constant weight (63.29) at 80 °C for 48 h and stored as described previously for CCPP.

2.2.3. Preparation of MSPP

To 200 g of previously ground and sieved DFB (300–250 µm particle size), 800 mL of 0.52 M aqueous magnesium sulfate (50.15 g) solution was slowly added and stirred to a uniform slurry. This slurry was uniformly mixed with a magnetic stirrer (rpm = 500) for 6 h, at 24 °C and left to stand for 24 h. Then, excess solution was filtered through Whatman number 1 filter paper, and the residue was washed four times each with 500 mL of deionized water, oven-dried at 1 atm pressure to constant weight to constant weight (216.47 g) at 80 °C for 48 h. Thus, ~16 g of MgSO₄ remain in the modified biochar at this stage. Then, to the magnesium sulfate-modified biochar, 800 mL of 5 M potassium hydroxide solution was slowly added while stirring (rpm = 500) to provide a uniform slurry for 6 h at 24 °C. This was aged for an additional 24 h at 24 °C, to allow MgO to form on the surface. The product was vacuum filtered through a Whatman number 1 filter paper and then oven-dried for 48 h at ~1 atm pressure and 80 °C to constant weight (~244.18 g). A 100 g amount of this modified Douglas fir biochar was mixed with 400 mL of 1.61 M L⁻¹ aqueous potassium dihydrogen phosphate while stirring to a homogeneous slurry. Stirring was continued for an additional 6 h at rpm = 500 at 24 °C and then the slurry was aged for 24 h at 24 °C. The excess solution was filtered through Whatman number 1 filter paper and the residue oven-dried at 1 atm to constant weight (149.6 g) at 80 °C for 48 h. The product, MSPP, was cooled to ambient temperature and kept in a tight container until use.

2.3. pH stabilization reaction time

The time needed for pH stabilization was determined following acid addition to all soil and biochar samples. Air-dried soil or biochar samples (DFB, CCPP, CAPP and MSPP) 2.5 g were added to a 50 mL polypropylene tube (in triplicate). To each sample, 0, 1 or 2 mL of 0.1 M HCl acid was added, and the total volumes were increased to 25 mL with deionized water. The samples were placed in a reciprocating shaker (200 rpm) at room temperature for 24 h. Then the slurry pH was measured after 24, 48, 72, 96, 120, 144, 168, 192 and 216 h using a Hanna pH meter (model HI 3221).

2.4. Determining pH and electrical conductivity

Biochar pH and electrical conductivity (EC) were determined by accurately weighing 5.0 g each of air-dried DFB, CCPP, CAPP or MSPP into 100 mL polypropylenes tubes (Singh et al., 2017). Deionized water (50 mL) was added to each tube, and they were shaken at 200 rpm for 1 h at 25 °C. After standing for 30 min, the pH and EC were determined using a Hanna pH meter and a Hanna edge electrical conductivity meter, respectively.

2.5. DFB, CAPP, CCPP and MSPP characterization

The alkalinity of DFB, CCPP, CAPP and MSPP were measured by the acid-base titration method described by (Xu et al., 2012). The alkalinity was expressed as mmol of H⁺ reacted per g of air-dried biochar, calculated from the quantity of hydrochloric acid consumed by biochar samples. To each biochar sample (0.5 g) in a 50 mL polypropylene tube, 20 mL of deionized water was added. This mixture was shaken for 2 h at 25 °C. The samples were titrated at 0.5 mL per min with 0.1 M HCl to the end point of pH 2.0. The alkalinity was obtained from the quantity of HCl consumed by each sample during the titration.

Acid groups on the biochars were analyzed by the Boehm method (Ellen et al., 2017). This assumes that NaHCO₃ neutralizes only carboxylic acid groups (pK_a ≤ 6.4), Na₂CO₃ neutralizes carboxylic acids and lactones (pK_a ≤ 10.3), and NaOH neutralizes all acids including phenolic groups (pK_a < 13). Approximately 1.0 g of each biochar sample

was placed in a 100 mL plastic bottle. Then, 50 mL of 0.05 M NaHCO₃, Na₂CO₃ or NaOH was added, and the mixtures were shaken 24 h at 25 °C. The supernatant was filtered, and 20 mL of each solution was titrated with 0.2 M HCl acid solution. Blank samples (no biochar added) were used for each base titrant. All treatments were analyzed in triplicate. The total surface acidity and the carboxylic acid fractions were calculated as moles neutralized by NaOH and NaHCO₃, respectively.

Previously oven-dried (105 °C) biochar 1.0 g samples were added to a pre-weighed crucible to measure the ash content by heating in a muffle furnace at 650 °C for at least 6 h. After cooling, the mass of crucibles and their contents were measured, and the ash content calculated from equation 1

$$\% \text{ ash content} = \frac{\text{Weight of ash (g)} \times 100}{\text{Original weight of samples (g)}} \quad (1)$$

The metal concentrations were determined by weighing 0.2 g of biochar samples in a crucible, then ashing in a muffle furnace for 8 h at 650 °C. After cooling to ambient temperature, 5.0 mL of HNO₃ acid and 2.0 mL of HCl acid were added to each vessel. The mixtures were heated at 150 °C on a hot plate to dryness. After cooling to ambient temperature, 10 mL of deionized water was added to dissolve the ash before filtering through Whatman number 1 filter paper. The filtrates were then analyzed for Mg, Ca, P, and K with an ICP-MS model (ELAN DRC II) after appropriate dilution with deionized water.

The surface morphologies were analyzed by scanning electron microscopy (SEM, JEOL JSM-6500 F FE-SEM operated at 5 kV). The elemental distributions on DFB, CAPP, MSPP and CCPP were measured using scanning electron microscopy-electron diffraction spectroscopy (SEM-EDS). The specific surface area, pore size diameter and average pore volume were measured by Brunauer–Emmett–Teller (BET) nitrogen adsorption method at 77.3 K using a Micromeritics Tristar II Plus Version 2.03 surface area analyzer. The quantities of crystalline compounds in the modified biochars were examined by powder X-ray diffraction with a Rigaku's Smartlab X-ray diffraction system using Cu-Kα (λ = 1.54 Å) radiation generated at 40 kV and 44mA. The XRD patterns were taken by scanning 2θ from 5° to 90° with 0.05° steps at a rate of 4° min⁻¹. The peaks were identified by matching in qualX 2.0 Software.

2.6. Thermogravimetric analysis (TGA)

Thermogravimetric analyses were performed with a DTG-Q50 device using 5 mg samples of DFB, CCPP, CAPP and MSPP. These were heated from room 25 °C to 1000 °C at a rate of 10 °C min⁻¹ in a nitrogen flow rate of 50 mL min⁻¹. The first derivative of the TGA curves were then calculated to establish the loss in mass over the temperature range used. The recalcitrance index (R₅₀) of the biochar samples was calculated using equation 2

$$R_{50, \text{sample}} = \frac{T_{50, \text{sample}} \times 100 \%}{T_{50, \text{graphite}}} \quad (2)$$

where, T_{50, graphite} and T_{50, sample} are the temperatures at which the graphite and biochar sample weight decreased by 50%, respectively (Wang et al., 2021).

2.7. ATR-FTIR analysis

DFB, CCPP, CAPP and MSPP (1.0 g) were oven-dried at 1 atm pressure at 60 °C for 24 h, ground and sieved to a 250–300 µm particle size. Surface functions were analyzed using a Nicolet 6700FT-IR instrument with an attenuated total reflectance (ATR) accessory. FTIR spectra from 400 scans were recorded in the wavenumber range 4000–500 cm⁻¹ with 2 cm⁻¹ resolution.

2.8. Determining soil buffering capacity and electrical conductivity

A sandy surface soil (0–20 cm) was collected from the Mississippi State University research farm, air-dried, homogenized, ground, and sieved through 2 mm mesh before analysis. Prior to use, the soil was analyzed for physical and chemical properties (Table S1), following the Lancaster Soil Test method described by (Cox, 2001). The soil had a pH of 5.64.

Soil buffering capacities were determined on 2.5 g samples in 50 mL polypropylene tubes, to which 0, 0.25, 0.5, 1, 2, 4, and 6 mL of 0.1 M HCl was added. In each tube, 0.05 M aqueous CaCl_2 was added to minimize variation of ionic strength. Deionized water was added to bring each total volume to 25 mL (ratio 1:10 soil: solution (wt./v)). All suspensions were equilibrated with shaking (200 rpm) for 24 h at 25 °C and then removed from the shaker to equilibrate for another 7 d, where samples were re-shaken at 200 rpm for 2 min daily to re-suspend the solids. After 8 of equilibration, pH was measured using the pH meter. Then soil buffering capacity was obtained from the slope of a plot of the amount of acid added against solution pH. Soil electrical conductivity was determined following method by (Mylavarapu et al., 2020). Briefly, 10 mL of deionized water was added to 5 g of air-dried soil (at room temperature) in a polypropylene tube (in triplicate). These slurries were equilibrated on a reciprocating shaker (200 rpm) for 4 h and filtered through Whatman no. 42 filter paper. The EC was measured as described for biochar in section 2.4.

2.9. Effect on soil buffering capacity and electrical conductivity of incorporating biochar

To assess the influence of incorporating biochar on soil buffering capacity/electrical conductivity, air-dried soil was mixed with biochar samples at a biochar:soil ratio of 0%, 10%, 30% and 50% (wt/wt). DI water was added to the mixtures to maintain water holding capacity near 80% of field capacity. After incubating at 25 °C for 30 d, soil/biochar was air-dried at room temperature, and pH buffering capacity and electrical conductivity were determined as for soil in section 2.8 above.

3. Results and discussions

3.1. Time required for pH stabilization

Following acid additions at amounts of 0 mmol $\text{H}^+ \text{kg}^{-1}$, 20 mmol $\text{H}^+ \text{kg}^{-1}$ and 40 mmol $\text{H}^+ \text{kg}^{-1}$, the pH stabilized within 72 h for MSPP and 96 h for neat soil, CCPP, and CCAP. The pH stabilized after 192 h for DFB. Also, the pH of MSSP after addition of 20 mmol $\text{H}^+ \text{kg}^{-1}$ did not differ from that of 0 mmol $\text{H}^+ \text{kg}^{-1}$ (Fig. 1a–e). In both cases, the pH values after 24–48 h were 10.9 but changed to 11 after 72–216 h.

The pH versus time plots for neat soil, MSPP, CCPP and CCAP were shown in Fig. 1. In each case the difference between stabilized pH and initial pH (after 24 h) ranged between 0 and 0.3 units. For Douglas fir biochar however, the difference was 1.70 and 1.23 for 20 mmol $\text{H}^+ \text{kg}^{-1}$ and 40 mmol $\text{H}^+ \text{kg}^{-1}$ addition, respectively (Fig. 1).

The pH stabilization of neat soil, CAPP, CCPP, MSPP, and Douglas fir biochar occurred within 72–192 h after acid addition. The stabilization time varied for each material. Variable stabilization times have been reported for compost and oak biochar in other titration experiments (Costello and Sullivan, 2014; Mukherjee et al., 2011). During compost titrations, pH stabilizes within 72 h after acid addition (Costello and Sullivan, 2014). Oak biochar pH stabilized within 2 h (Mukherjee et al., 2011). Since stabilization time depends on the material, the longest time (192 h) was chosen for determining pH buffering capacities of neat soil and soil-biochar mixtures.

3.2. Biochar pH and electrical conductivity

The modified biochars exhibited significantly increased pH (Fig. 2) and EC (Table 1) values.

The largest EC increase versus DFB was achieved with MSPP (1734 $\mu\text{S cm}^{-1}$). The other EC increases over DFB were 68 $\mu\text{S cm}^{-1}$ for CCAP and 1074 $\mu\text{S cm}^{-1}$ CCPP. Similarly, MSPP, CCAP, and CCPP resulted in pH increases of 3.4, 1.3, and 0.3 units, respectively, versus DFB. Numerous studies have reported biochar pH and EC increases are related to its ash content (Dume et al., 2015; Wang et al., 2014). In this study, the electrical conductivities were positively correlated with biochar's ash content ($r = 0.75$). Moreover, the ash contents were positively correlated to Mg, Ca, K, and P concentrations ($r \geq 0.4$). Therefore, the rise in EC following modification is ascribed to the increased salt content in the modified biochar. Similarly, the pH increase is attributed to rise in concentration of Ca^{2+} , Mg^{2+} , and K^+ after modification.

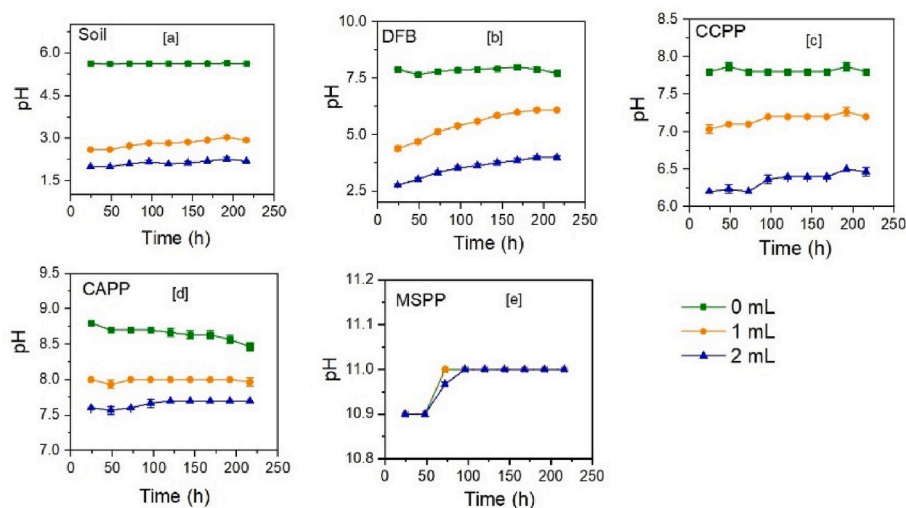


Fig. 1. Time required to reach a stable pH after dilute acid addition of 0 mmol $\text{H}^+ \text{kg}^{-1}$, 20 mmol $\text{H}^+ \text{kg}^{-1}$ and 40 mmol $\text{H}^+ \text{kg}^{-1}$ for a) neat soil (Soil), b) Unmodified Douglas fir biochar (DFB), c) Douglas fir biochar treated with CaCl_2 and KH_2PO_4 (CCPP), d) Douglas fir biochar treated with CaCO_3 and $(\text{NH}_4)_2\text{HPO}_4$ (CAPP) and e) Douglas fir biochar treated with MgSO_4 , KOH and KH_2PO_4 (MSPP). Values used are mean, $n = 3$ and error bars shown as standard error of the mean.

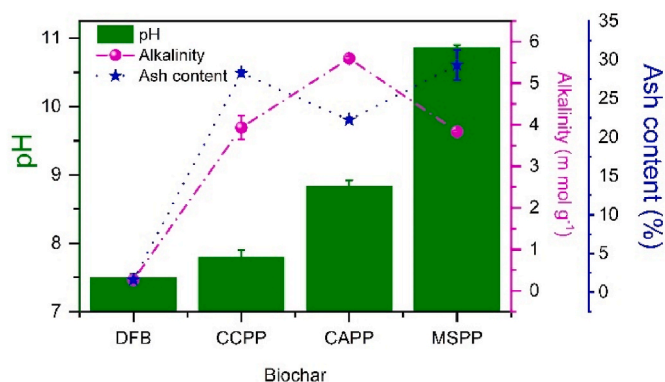


Fig. 2. Biochar alkalinity, ash content and pH before (DFB) and after modifying DFB with $\text{CaCl}_2 + \text{KH}_2\text{PO}_4$ (CCPP), $\text{CaCO}_3 + (\text{NH}_4)_2\text{HPO}_4$ (CCAP) and $\text{MgSO}_4 + \text{KOH} + \text{KH}_2\text{PO}_4$ (MSPP). (Values shown are mean of $n = 3$, error bars shown as standard error of the mean).

3.3. DFB, CAPP, CCPP and MSPP characterization

Total alkalinity varied extensively among the treated biochars treatments ($0.27\text{--}5.60 \text{ mmol g}^{-1}$), with CCAP and DFB having the highest and lowest values, respectively (Fig. 2). Biochar pH measured in water rose with increasing total alkalinity ($r = 0.43$), but regression analysis indicated this variation was insignificant ($r^2 = 0.18$, P value = 0.5). The pH values for DFB, CCPP, CAPP and MSPP measured in water were 7.5 ± 0.1 , 7.8 ± 0.8 , 8.8 ± 0.2 and 10.9 ± 0.1 , respectively.

Boehm titration of the acidic surface functions (lactonic, carboxylic, and phenolic) of DFB and all modified biochars were given in Table 1. The abundance of carboxyl groups were about equal in DFB and CAPP, and somewhat less in CPP and MSPP. The lactones groups decreased in the order $\text{DFB} > \text{CAPP} > \text{MSPP} > \text{CCPP}$. The phenolic groups increased in the order $\text{DFB} \approx \text{MSPP} < \text{CAPP} < \text{CCPP}$. The total of all acidic functions followed the order $\text{CCPP} > \text{DFB} = \text{CAPP} > \text{MSPP}$ with range from 0.05 to 0.03 mmol g^{-1} . Biochar's pH dropped as the amount of all surface acid functional groups rose with correlation coefficients of ($r = 0.5$, 0.8 and 0.5) for carboxylic, lactonic and phenolic groups, respectively.

The DFB modifications significantly enhanced both its metal concentrations (Table 1) and ash content (Fig. 2). MSPP had the largest increase in ash content (from 1.6 to 29.3%). Ash contents for CCPP increased from $1.6\text{--}28.3\%$ and CCAP from 1.6 to 22.2% , respectively. Ash contents for all biochars were positively correlated to Mg, Ca, K, and P concentrations ($r \geq 0.4$). Regression analysis indicated a positive, but insignificant correlation between ash contents and pH (P value = 0.4 , $r^2 = 0.35$).

An insignificant difference in pH of DFB and CCPP existed, despite the variation of their alkalinities. The highest (0.05 mmol g^{-1}) and lowest (0.03 mmol g^{-1}) total acidic functions belong to CCPP and MSPP, respectively, while the total quantity of acid functions on DFB were comparable to that on CCAP (0.04 mmol g^{-1}). The total acid functionality was mostly due to the high pK_a (>7) phenolic groups especially for

MSPP and CAPP. Thus, their contribution to pH can be low. The lower pH of DFB versus CCAP and MSPP results from the greater contribution of its low pK_a lactones ($\text{pK}_a \sim 4$ to 7) and carboxylic acid ($\text{pK}_a \sim 2$ to 4) groups. The higher alkalinity of the modified biochars versus DFB could be due to a rise in base saturation after modification. Since biochar pH is influenced by both acid functional groups and nutrient elemental concentrations (Gezahegn et al., 2019), the correlation between pH and total alkalinity suggests that pH may not solely be a result of biochar alkalinity.

Boehm titration indicated a reduction in carboxylic acid and lactone groups and an increase in phenolic groups on modification of DFB. Hence, enhancing phenolic concentration by modification could raise biochar pH. Furthermore, impregnation of biochar with basic metal salts increased its metal concentrations (Mg, Ca and K) and ash contents as shown by positive correlations between ash contents and Mg, K, Ca, and P concentrations ($r \geq 0.4$). Previous studies linked biochar's pH, ash content, and EC to their mineral metal concentrations (Gezahegn et al., 2019; Rehrh et al., 2014). The increase in ash content after modification comes from the additional amounts of inorganics added. The enhanced concentrations of K, Mg, P and ash in MSPP versus DFB, CCAP, and CCPP explains its higher pH and EC. Gezahegn et al. (2019) analyzed biochars from 19 wood feedstocks, confirming that increases in pH, EC and ash content were highly correlated to biochar's mineral concentrations, particularly Ca and K. Therefore, results from this study suggest that biochar's alkalinity/liming value are largely controlled by its ash content (particularly Ca, Mg, and K), and by pH to a smaller degree. Accordingly, the low alkalinity shown by DFB despite its high pH indicate a smaller pH effect on biochar's alkalinity. These results agree with those of (Neina et al., 2020).

DFB, CCPP, CAPP and MSPP displayed heterogeneous surface morphologies.

So, SEM images were taken from three different locations (Fig. 3).

DFB exhibited large internal pores originating from the wood structure. The xylem and phloem vascular structure have been maintained by the carbon matrix in DFB's images. Upon modification to CAPP, CCPP and MSPP, the morphology appeared more complex due to mineral aggregates on the surfaces. These mineral phases partially filled or blocked pores, lowering CAPP, CCPP and MSPP surface areas. BET surface areas (Table S2) confirmed the reduction of DFB's surface area by ~ 254 , ~ 264 and $\sim 612 \text{ m}^2 \text{ g}^{-1}$ after modification to CAPP, CCPP and MSPP, respectively.

SEM-EDX elemental surface region compositions of DFB, CAPP, CCPP and MSPP were taken from three locations in each to obtain a representative analysis (Fig. S1). SEM-EDX interrogates to a depth of $\sim 5.3 \mu\text{m}$ with a spot diameter of $4\text{--}6 \mu\text{m}$. DFB exhibited, average C, O, P, Ca, K and Mg values for the three locations of ~ 87.04 , ~ 9.47 , ~ 0.84 , ~ 0.71 , ~ 1.54 , $\sim 0.10\%$, respectively. After modifying to CAPP, CCPP and MSPP, the averaged analyses of three locations gave ~ 76.31 , ~ 64.67 and $\sim 31.12 \text{ C } \%$, respectively. The corresponding values for % O, P, Ca, K and Mg were shown in Table 2.

The average molar Ca/P ratios for CAPP and CCPP were ~ 0.93 and ~ 0.88 , respectively. The theoretical molar Ca/P for CaHPO_4 , $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$ and $\text{Ca}_{10}(\text{PO}_4)_6 \cdot (\text{HO})_2$ are 1.00 , 1.00 , 1.33 and 1.67 , respectively (Mekmene et al., 2009), suggesting

Table 1

Biochar's electrical conductivity (EC), acid functional groups amount and mineral concentrations.

Biochar ^a	EC ($\mu\text{S cm}^{-1}$)	Acid functional groups (mmol g^{-1})				Metal concentrations (g kg^{-1})			
		phenolic	lactonic	carboxylic	Total	Mg	Ca	K	P
DFB	134.2 ± 3.21	0.023 ± 0.008	0.013 ± 0.008	0.004 ± 0.00	0.04 ± 0.02	0.95 ± 0.04	3.40 ± 0.14	0.45 ± 0.03	0.01 ± 0.00
CCPP	1208.7 ± 5.21	0.037 ± 0.012	0.011 ± 0.006	0.003 ± 0.00	0.05 ± 0.02	0.81 ± 0.00	110.13 ± 7.07	4.43 ± 0.06	50.23 ± 0.71
CCAP	201.8 ± 3.63	0.031 ± 0.012	0.008 ± 0.004	0.004 ± 0.00	0.04 ± 0.02	0.55 ± 0.01	130.53 ± 0.72	0.63 ± 0.07	10.95 ± 0.21
MSPP	1868.0 ± 40.5	0.024 ± 0.008	0.005 ± 0.004	0.003 ± 0.00	0.03 ± 0.01	23.64 ± 0.22	0.14 ± 0.01	68.50 ± 0.71	0.18 ± 0.01

^a DFB: Untreated Douglas fir biochar; CCPP: $\text{CaCl}_2 + \text{KH}_2\text{PO}_4$ treated Douglas fir biochar; CCAP: $\text{CaCO}_3 + (\text{NH}_4)_2\text{HPO}_4$ treated Douglas fir biochar; MSPP: $\text{MgSO}_4 + \text{KOH} + \text{KH}_2\text{PO}_4$ treated Douglas fir biochar. Values shown are calculated using mean of $n = 3$, error bars shown as standard deviation.

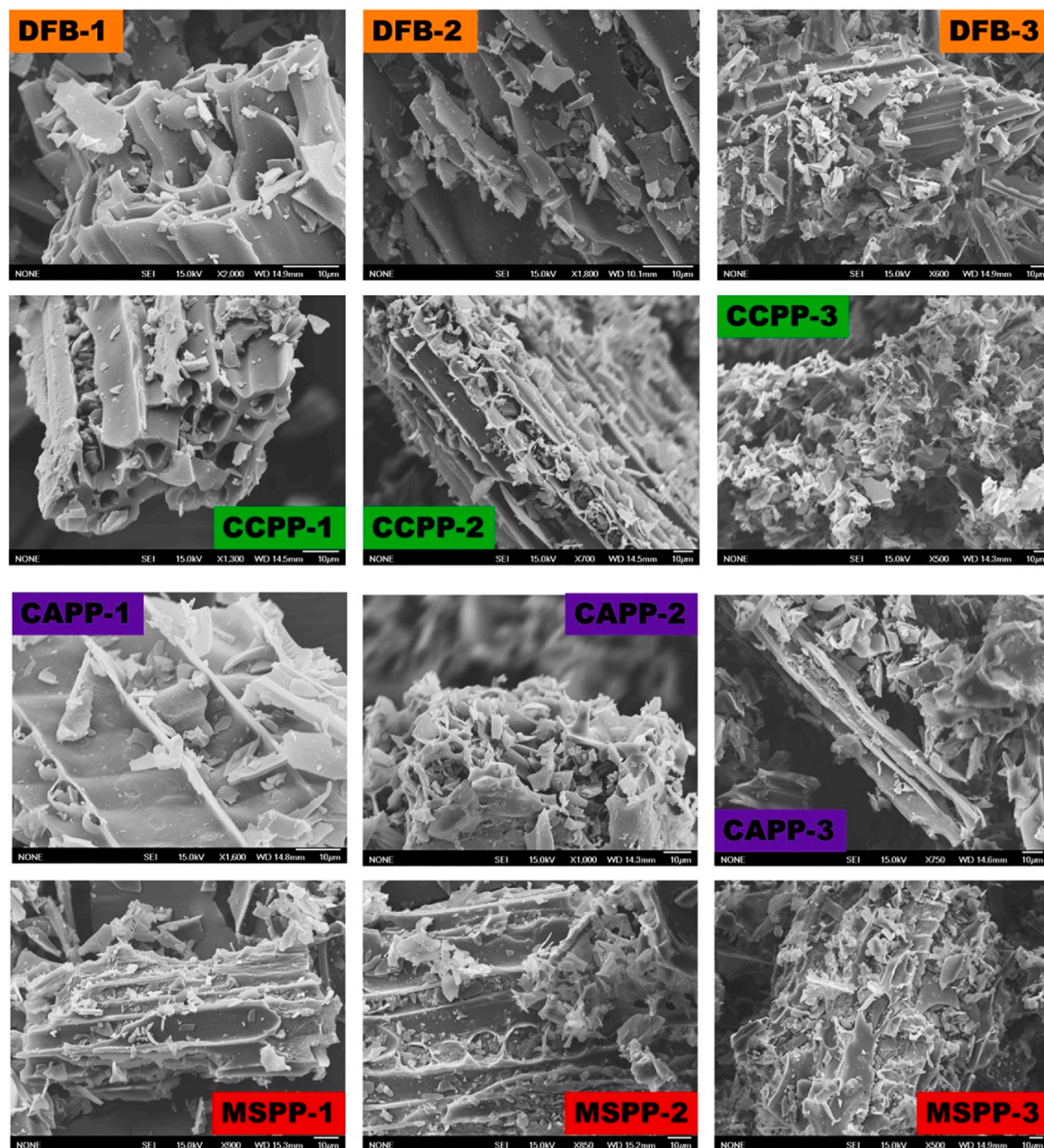


Fig. 3. SEM micrographs of DFB, CCPP, CAPP and MSPP from different points of the sample's surfaces.

Table 2

Average percent elemental composition analysis from three locations.

Biochar ^a	Elemental composition (%)				
	O	P	Ca	K	Mg
CAPP	9.66	5.85	7.02	7.25	0.00
CCPP	20.29	6.41	1.17	0.79	24.40
MSPP	33.07	5.12	0.11	0.1	5.55

^a CCPP: $\text{CaCl}_2 + \text{KH}_2\text{PO}_4$ treated Douglas fir biochar; CCAP: $\text{CaCO}_3 + (\text{NH}_4)_2\text{HPO}_4$ treated Douglas fir biochar; MSPP: $\text{MgSO}_4 + \text{KOH} + \text{KH}_2\text{PO}_4$ treated Douglas fir biochar.

phosphate deposited mostly as CaHPO_4 and $\text{CaHPO}_4 \cdot \text{H}_2\text{O}$ on CAPP and CCPP surfaces. XRD analyses of MSPP revealed phosphate occurred as $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ and $\text{Mg}_3(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$. These depositions raise the amount of surface oxygen. In contrast, the carbon contribution drops as

the surface is partly covered by mineral depositions. Pore blockages at the surface agrees with the decline in MSPP, CCPP and CAPP BET surface area compared to DFB (Table S2). Pore blockages by surface deposition was previously reported by (Zhang et al., 2021).

The XRD analyses of DFB, CCPP, MSPP and CAPP (Fig. S2) identified the mineral species deposited. DFB XRD spectra showed two broad peaks like those of layered graphene between $2\theta = 20^\circ\text{--}30^\circ$ and $40^\circ\text{--}50^\circ$, attributed to graphitic-like diffraction created as lignocellulosic structures are partly aromatized during pyrolysis (Siburian et al., 2018).

New peaks inorganic appeared in MSPP, CCPP and CAPP. In MSPP, major diffractions were observed due to MgO at $2\theta = \sim 43^\circ$ [JCPDS file No. 45-0946] (Khodair et al., 2016), $\text{Mg}(\text{OH})_2$ at $2\theta \sim 19^\circ$ and $\sim 38^\circ$ [JCPDS card no. 00-007-0239]. (Kumari et al., 2009; Saoud et al., 2014), hydrated $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ [JCPDS No. 72-0023] and $\text{Mg}_3(\text{PO}_4)_2 \cdot 5\text{H}_2\text{O}$ [JCPDS No. 35-0329] (Qian et al., 2016). Both CAPP and CCPP exhibited major diffractions at $2\theta = \sim 11.6^\circ, \sim 21^\circ, \sim 28.4^\circ, \sim 32^\circ, \sim 40.6^\circ\text{--}46.8^\circ, \sim 49.9^\circ$ and $\sim 64.2^\circ$ matching those of hydroxyapatite (HAP,

$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ [JCPDS card Number 09-0432] (Arellano-Jiménez et al., 2009; Sakamoto et al., 2016). CCPP additional peaks at $2\theta = 9.4^\circ$, 26° and 53° matched octacalcium phosphate (OCP, $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$), [ICDD number 261056] (Sakamoto et al., 2016).

CAPP also contained calcium carbonate (CaCO_3) diffractions at $2\theta = \sim 29.4^\circ$, $\sim 39.6^\circ$ and $\sim 48.4^\circ$ [ICDD PDF No. 5-0586] (Hazzat et al., 2020) and dibasic calcium phosphate dihydrate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, Brushite) diffractions appeared at $2\theta = \sim 23^\circ$, $\sim 29^\circ$ and $\sim 31.4^\circ$ [ICDD PDF No. 09-077] (Hazzat et al., 2020). Other amorphous P-containing species might be present on CAPP, CCPP and MSPP but would not be observed by XRD due to their poor crystalline order.

3.4. Thermogravimetric analysis (TGA)

TGA thermograms of DFB, CAPP, CCPP and MSPP conducted under nitrogen at $10^\circ\text{C min}^{-1}$ are shown in Fig. 4 [a].

All samples loose mass going to 1000°C due to progressive carbonization. CCPP did not differ much from DFB but CCAP underwent a sharp weight loss - at $\sim 700^\circ\text{C}$ perhaps because of excess CaCO_3 in this sample undergoing its well-known decomposition reaction to CaO (Georgieva et al., 2013; Ma et al., 2019). The present of CO_3^{2-} was also detected by FTIR at 2370 cm^{-1} (Fig. 4 [b]). Its limited CaCO_3 content prevents a larger mass loss. Similar result was also reported by (Kumar et al., 2015). MSPP exhibits major weight losses from 350 to 1000°C after minor weight losses from 30 to 350°C . MSPP showed the largest first weight loss ($\sim 6.2\%$) between 30 and 242°C likely due to water of hydration losses from inorganics. MSPP also contains KOH which above 600°C causes activation reactions resulting in carbon losses, pore diameter and surface area increases. The low temperature weight losses for CCPP and DFB were comparable (1.3%) occurring between 30 – 170°C and 97.2 – 180°C , respectively. CCAP showed greatest thermal stability at the start with an initial weight loss of 1.9% between 326.6 and 383°C . In all cases, the initial weight loss involves elimination of chemically unbound moisture. MSPP undergoes major weight loss at $\sim 350^\circ\text{C}$ which accelerates above 700°C . Major weight loss for DFB, CCAP, and CCPP occurred at much greater temperatures ($>600^\circ\text{C}$). A drop in biochar thermal stability after MgO impregnation is known (Carneiro et al., 2018). The calculated recalcitrance index (R_{50}) for MSPP was ~ 0.99 . However, the recalcitrance index (R_{50}) for DFB, CCAP and CCPP were not calculated because the weight loss of 50% was not realized up to 1000°C . A biochar with a recalcitrance index (R_{50}) > 0.7 is considered a class A biochar with carbon sequestration potential similar to graphite (Harvey et al., 2012). The recalcitrance indices (R_{50})

corresponding to DFB, CCPP and CAPP are likely to be > 1 . MSPP's reduced recalcitrance index (R_{50}) due to its higher alkali content and known for KOH activation. R_{50} value of wheat straw biochar increased from ~ 0.46 to ~ 0.55 after washing to remove alkali contents (Windeatt, 2015). Mineral content analysis followed the orders MSPP $>$ CCPP $>$ CAPP $>$ DFB (for K), MSPP $>$ DFB $>$ CCPP $>$ CAPP (for Mg^{2+}), CAPP $>$ CCPP $>$ DFB $>$ MSPP (for Ca^{2+}) and CCPP $>$ CAPP $>$ MSPP $>$ DFB (for P).

3.5. FTIR-ATR analysis

FTIR-ATR analyses (Fig. 4 [b]) were run to identify surface functional group changes on treated biochars. The FTIR-ATR spectra for DFB, CCPP (CaCl_2 plus KH_2PO_4 modified Douglas fir biochar), CCAP (CaCO_3 plus $(\text{NH}_4)_2\text{HPO}_4$ modified Douglas fir biochar) and MSPP (MgSO_4 plus KOH plus KH_2PO_4 modified Douglas fir biochar) are shown in (Fig. 4 [b]).

Weak absorptions between 3670 and 3550 cm^{-1} are due to hydrogen-bonded hydroxy groups in these are in the chars phenol, $\text{Mg}(\text{OH})_2$ and hydroxyapatite (Bekiaris et al., 2016). Bands at 2971 and 2887 cm^{-1} were assigned to asymmetric and symmetric sp^3 hybridized C – H stretches (Coates, 2000). C – O stretching at 1252 , 1150 , 1149 cm^{-1} were assigned carboxylic acids, variscite and phenols respectively. Bands due to CO_3^{2-} ions occurred at 1382 cm^{-1} , 880 , 860 and 711 cm^{-1} . Absorption at 638 , 622 and 613 cm^{-1} were attributed to stretching of Mg–O–Mg bonding in $\text{Mg}(\text{OH})_2$. Phosphates were observed at 1072 and 950 cm^{-1} due to P – O symmetric and asymmetric stretching, respectively. P – O H vibrations ascribed to HPO_4^{2-} occurred at 1588 cm^{-1} (Assaoudi et al., 2007; Bas et al., 2009).

3.6. Soil buffering capacity and electrical conductivity

Soil buffering capacity is the amount of acid required to reduce the pH of a unit mass of soil by 1 unit (Huang et al., 2009). Buffering capacity was obtained from the slope of the linear regression fit of the amount of H^+ ion added to soil versus pH responses.

The soil pH decreased in proportion to the quantity of acid added ($r^2 > 0.9$). The soil buffering capacity was $8.00\text{ mmol kg}^{-1}\text{ pH}^{-1}$. This capacity can be influenced by CEC, organic matter and clay content which affect protonation and deprotonation in soil. The sandy loam soil used here was low in clay and organic matter contents. Its pH buffering capacity is primarily affected by the variation in CEC. Soil pH buffering capacities determined from HCl addition in 20 different soil samples

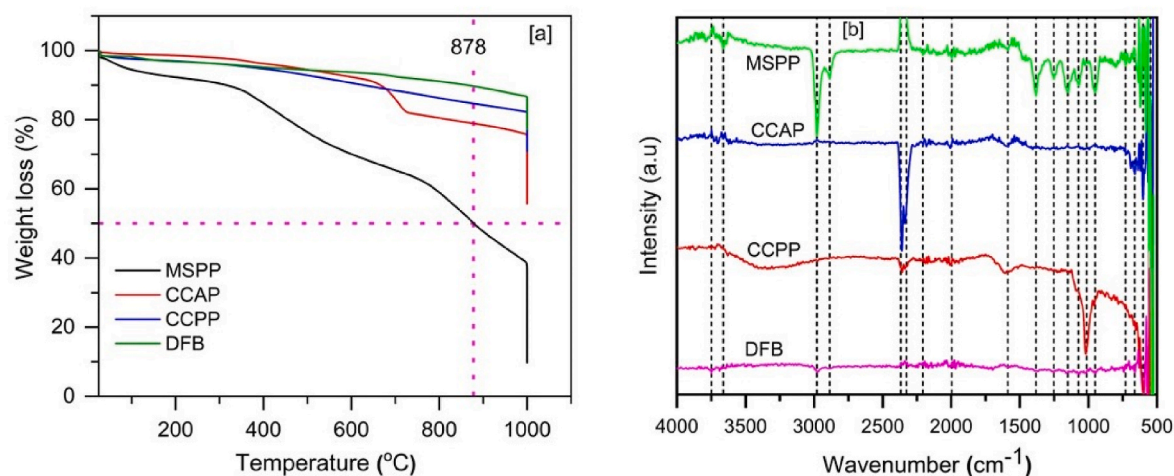


Fig. 4. TGA thermograms at heating rate of $10^\circ\text{C min}^{-1}$ for heating temperature range of 25 – 1000°C [a] and FTIR-ATR spectra [b] for unmodified Douglas fir biochar (DFB), Douglas fir biochar treated with CaCl_2 and KH_2PO_4 (CCPP), Douglas fir biochar treated with CaCO_3 and $(\text{NH}_4)_2\text{HPO}_4$ (CCAP) and Douglas fir biochar treated with MgSO_4 , KOH and KH_2PO_4 (MSPP).

ranged from 3.2 to 57.7 mmol kg⁻¹ pH⁻¹ unit (Aitken and Moody, 1994). Buffering capacities varied from 9.1 to 32.1 mmol kg⁻¹ pH⁻¹ in 24 acidic soils signifying that soil properties impact pH buffering capacity (Xu et al., 2012).

3.7. The effects of incorporating biochar on soil buffering capacity and electrical conductivity

The pH response of our soil/biochar mixtures to acid addition were fitted with a linear regression function. The regression results were significant for CCPP, CCAP, and MSPP samples (p value ≤ 0.01 with $r^2 \geq 0.9$) but insignificant for the unamended soil and soil amended with DFB. The buffering capacities ranged from $(8.23 \pm 0.17 - 82.63 \pm 1.42 \text{ mmol kg}^{-1} \text{ pH}^{-1})$ over all samples assessed. The highest and lowest improvements were recorded with CCAP and DFB, respectively (Fig. 5a).

Both pH buffering capacity and the cation exchange capacity (Fig. 5a and 5b, respectively) increased with rise in quantity of biochar added to soil (50% > 30% > 10% > 0%). However, the increase in the buffering capacity for soil amended with DFB was much smaller than the increases induced by CCPP, CAPP, and MSPP.

Oxygen-containing groups on biochar surfaces buffer acid soil by protonation and deprotonation at low and high pH, respectively. The modified biochars contain added oxides, hydroxides and carbonates of bases such as Mg, K, and Ca which enhance their ash content, alkalinity, and pH (Xu et al., 2012). DFB had the lowest alkalinity, ash content, and pH (Fig. 2). Since biochar's buffering capacity is associated with its alkalinity (Berek and Hue, 2016; Mukome et al., 2013), the low buffering capacity of DFB is due to its low concentrations of basic cations and alkalinity relative to CCPP, CAPP and MSPP. Improvement in both alkalinity and pH buffering capacity followed the order CCAP > CCPP > MSPP > DFB (Figs. 2 and 5a, respectively). Residual soil CEC followed the order CAPP > MSPP > CCPP > DFB (Fig. 5b). Also, the residual soil CEC was highly correlated ($r \geq 0.9$), with the soil buffering capacity (Fig. S3). MSPP had higher concentrations of K⁺ and Mg²⁺, but greater concentrations of Ca²⁺ were present in CCAP and CCPP than MSPP. Therefore, Ca²⁺ concentrations in biochar seem to exert a greater influence on alkalinity and buffering capacity than Mg²⁺ and K⁺. The affinity for exchange sites varies for different cations based on their charge and hydrated radius size (Blume et al., 2015). The higher the charge, the stronger the ion is attracted by electrostatic forces to the negatively charge surface. For example, Al³⁺ > Mg²⁺ > Na⁺. Hence, Ca²⁺ is preferred to Mg²⁺ and K⁺ because of its smaller effective hydration radius (Unsw, 2007) and larger charge density. In addition,

calcium hydroxide has a greater water solubility than magnesium hydroxide providing more available base. Magnesium hydroxide has a larger lattice energy than calcium hydroxide lowering its solubility since more energy is required for it to dissolve. Since pH buffering capacity depends on cation exchange sites, soil additives containing Ca²⁺ are likely to create greater impacts than Mg²⁺ and K⁺ additives. Thus, Ca²⁺ benefits from greater exchange site affinities and lower lattice energy.

Incorporating biochar in soil significantly increased soil electrical conductivity (Fig. 6).

The EC increase was greater in modified biochar-amended soil than by adding DFB because increased salt concentrations released to the soil raises EC. Modified P-enriched biochar (CCPP, CCAP and MSPP) release the metal cation counter ions to HPO₄²⁻ and H₂PO₄⁻. Overall, greater metal concentrations and ash contents are released by the P-enriched biochars than DFB. Previously, increased soil EC was reported following biochar amendments (Shah et al., 2017), but this influence depended on the biomass feedstock used. In this study, EC values were within the

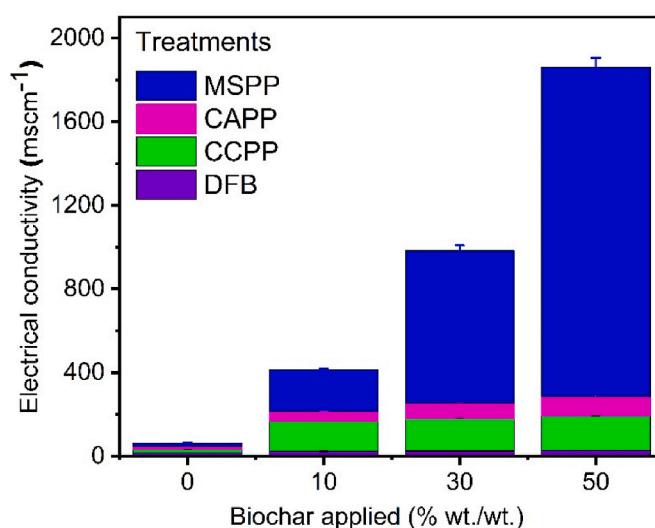


Fig. 6. Impact of biochar amendment on soil electrical conductivity (EC). DFB = unmodified Douglas fir biochar, CCPP = Douglas fir biochar modified with CaCl₂ + KH₂PO₄, CCAP = Douglas fir biochar treated with CaCO₃ + (NH₄)₂HPO₄, and MSPP = Douglas fir biochar modified with MgSO₄ + KOH + KH₂PO₄. (Values are average of n = 3. Error bars shown as SEM).

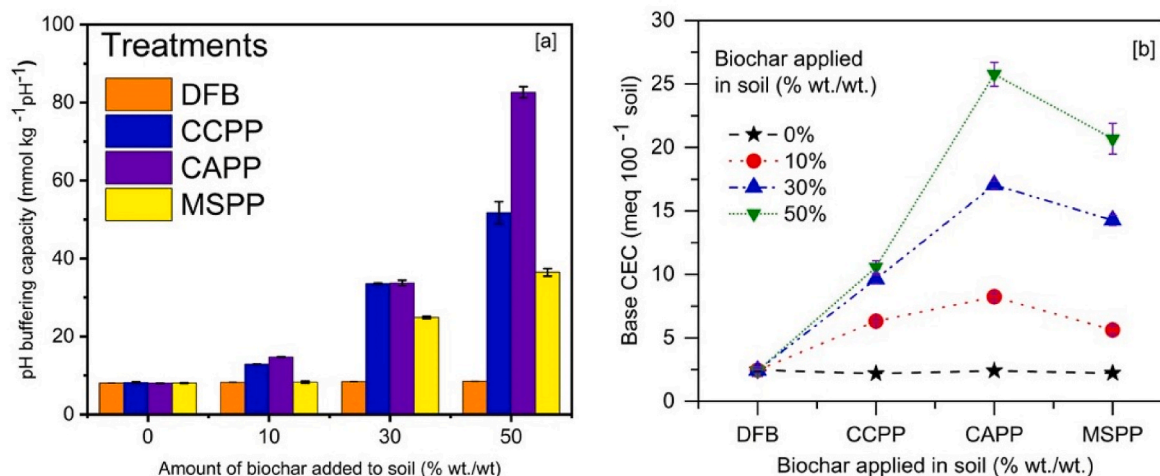


Fig. 5. Influence of biochar amendment on; (a) the soil pH buffering capacity (BC) and (b) Cation exchange capacity (CEC) after a 30-day incubation with DFB = unmodified Douglas fir biochar, CCPP = Douglas fir biochar modified with CaCl₂ + KH₂PO₄, CCAP = Douglas fir biochar treated with CaCO₃ + (NH₄)₂HPO₄, and MSPP = Douglas fir biochar modified with MgSO₄ + KOH + KH₂PO₄. (Values used = average of 3 replicates, errors bars shown as Standard error of the mean).

non-saline range of 0–2000 μscm^{-1} similar to those previously reported by (Lech et al., 2016), indicating that P-enriched biochars can be used for soil amendment.

3.8. Nutrient release to soil

The extractable nutrient concentrations increased with the amount of biochar added (Fig. 7 a-d).

MSPP and CCPP released increasing amounts of extractable P, Ca, Mg and K that were highly correlated to the quantity of biochar applied ($r > 0.9$). CAPP treatments released P, Ca and K amounts that were highly correlated to the amount of biochar applied ($r > 0.9$) but Mg gave a negative correlation ($r = \sim -0.6$) as the mass of biochar increased. DFB soil treatments gave positive, K and Mg correlations to the biochar quantity ($r = \sim 0.9$ and ~ 0.7 , respectively), but increasing the amount of DFB did not significantly affect P concentrations ($r = -0.009$). Also, the extractable calcium quantity decreased with increasing amount of added DFB ($r = -0.9$).

The extractable nutrient concentration is one indication of the nutrient quantity that would be released to soil following application of a given additive. This increase of extractable P, Ca, Mg, and K versus the rising amount of biochar added is one measure of the fertilizer potential for these three P-enriched biochars. In addition, MSPP treatments provided significantly greater extractable K concentrations, but Ca concentration was smaller than those from CCPP and CAPP treatments (Fig. 7a, b, c & d). The enhanced Ca concentrations from CCPP and CAPP treatments causes the higher alkalinity observed with CCPP and CAPP additions and role of Ca in regulating pH buffering capacity discussed in section 3.8. Furthermore, the negative correlations linked to DFB reaffirms its low ash contents, EC, alkalinity and pH buffering ability.

4. Conclusions

Incorporating modified P-enriched Douglas fir biochars in an acidic soil increased pH buffering capacity. This buffering capacity improvement was larger for soil amended with biochar modified with calcium-containing salts. The pH buffering capacity increased by 84.8, 58.3, 3.0 and 2.5%, after amendments with 10% CAPP, CCPP, MSPP and BFB, respectively. The lower lattice energy associated with calcium hydroxides versus magnesium hydroxide is the possible reason for the greater buffering capacity rise with high Ca^{2+} contents. Also, Ca^{2+} has greater affinity for cation exchange sites compared to Mg^{2+} , and K^+ , which is an advantage for biochar treated with calcium salts. The three modified Douglas fir biochars (CCPP, CAPP and MSPP) provided increased pH, ash content (P, K, Mg and Ca), and alkalinity, while delivering phosphate to soil. Amendment of acidic soils with modified P-enriched biochar provides simultaneous liming and fertilization benefits. Overall, modification of Douglas fir biochar had little effect on P-enriched biochar thermal stability. However, high potassium contents promote biochar weight loss at very high temperatures, resulting in a reduced recalcitrance index. The biological stability of P-enriched Douglas fir biochar to prove its usefulness in carbon sequestration should be further assessed.

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1. Beatrice Arwenyo – project manipulation. Worked with students and faculty. Department of Chemistry, Mississippi State University,

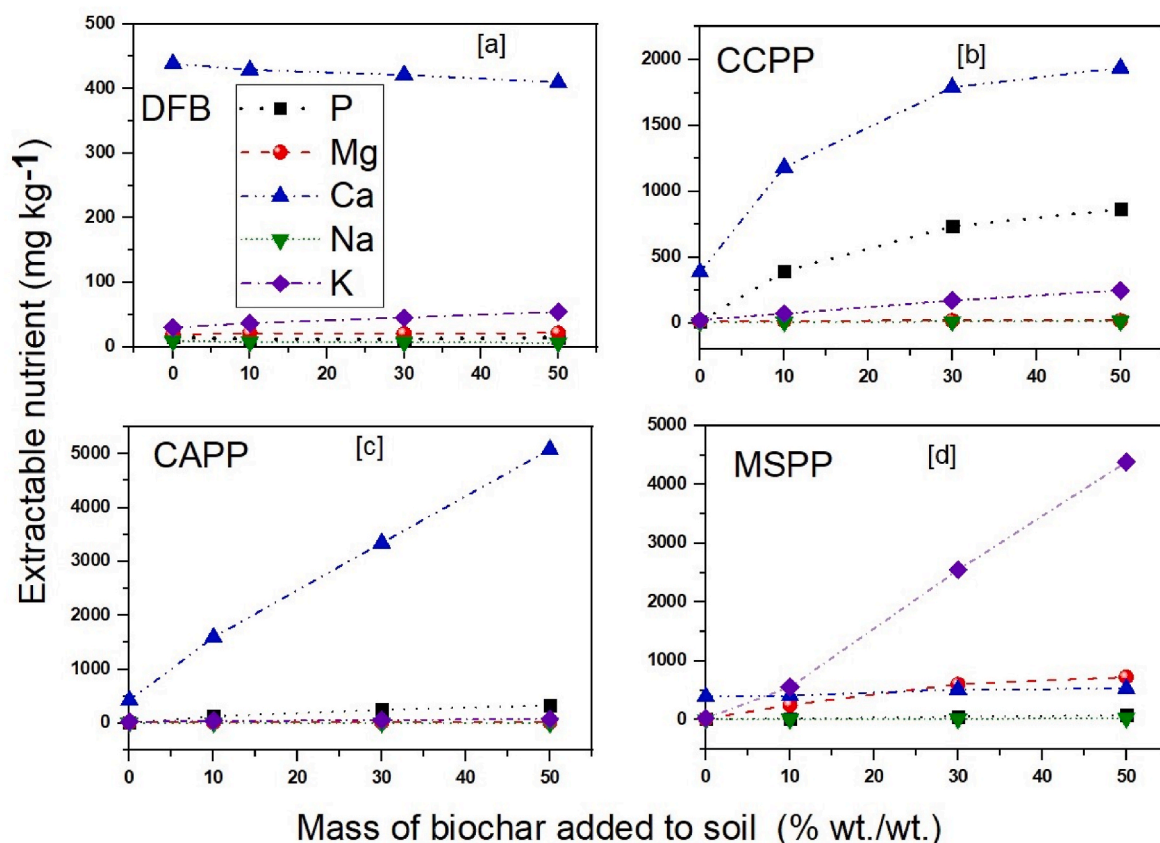


Fig. 7. Extractable nutrients (P, Mg, Ca, Na & K) after incubating soil with different masses of (a) DFB, (b) CCPP, (c) CAPP and (d) MSPP biochar (%wt./wt.).

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Author contributions

Arwenyo Beatrice: Designed the study. data collection, analyzed the data, wrote the manuscript. Jac J. Varco: Editing and suggested experiment. Andrew Dygert: performed the experiments. Sydney Brown: contributed to sample preparation. Charles U. Pittman Jr.: Editing and worked out almost all the technical details. Todd Mlsna: Editing and technical guidance.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jenvman.2023.117863>.

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